Fe(I)-mediated reductive cleavage and coupling of CO_2: An $Fe^{II}(\mu\text{-}O,\mu\text{-}CO)Fe^{II}$ core

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Supporting Information

Experimental Section.

General Considerations. All syntheses reported were carried out using standard dry-glove box and Schlenk techniques in the absence of water and dioxygen, unless otherwise noted. Benzene, petroleum ether, tetrahydrofuran, diethyl ether, and toluene were degassed and dried by sparging with N_2 gas followed by passage through an activated alumina column. All solvents were stored over 3-Å molecular sieves. Deuterated benzene, THF and toluene were purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze-pump-thaw cycles, and dried over 3-Å molecular sieves or powdered activated alumina (THF). Solvents were frequently tested using a standard solution of sodium benzophenone ketyl in tetrahydrofuran to confirm the absence of oxygen and moisture. $TlPF_6$ and $FeCl_2$ were dried *in vacuo* for 12 to 24 h to remove moisture. TMEDA (tetramethylethylenediamine) and $CyCH_2Br$ were degassed and stored over 3 Å sieves. All other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were recorded on Varian Mercury 300 MHz instruments at ambient temperature unless otherwise stated. ^1H and ^{13}C NMR chemical shifts were referenced to residual solvent. ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4. Elemental Analyses were performed by Desert Analytics, Tuscon, AZ. X-ray diffraction experiments were carried out by the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer. Solution magnetic moments were

measured using Evans' method.[1] UV/vis/NIR measurements were taken in THF on a Cary 500 UV/vis/NIR spectrophotometer using a 0.1 cm quartz cell with a Teflon stopper.

EPR Measurements. X-band EPR spectra were obtained on a Bruker EMX spectrometer equipped with a rectangular cavity working in the TE_{102} mode. Variable temperature measurements were conducted with an Oxford continuous-flow helium cryostat (temperature range 3.6 - 300 K). Accurate frequency values were provided by a frequency counter built in the microwave bridge. Solution spectra were acquired in tetrahydrofuran and sample preparation was performed under a nitrogen atmosphere.

Electrochemistry. Electrochemical measurements were carried out in a glove box under a dinitrogen atmosphere in a one-compartment cell using a CH Instruments electrochemical analyzer. A glassy carbon electrode and platinum wire were used as the working and auxiliary electrodes, respectively. The reference electrode was $Ag/AgNO_3$ in THF. Solutions (THF) of electrolyte (0.40 M $[^nBu_4N][PF_6]$) and analyte (2 mM) were also prepared in the glove box.

X-ray Crystallography Procedures. X-ray quality crystals were grown as indicated in the experimental procedures per individual complex. The crystals were mounted on a glass fiber with Paratone N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package.

Syntheses of Compounds.

Synthesis of $MeP(CH_2Cy)_2$: Magnesium coils (6.15 g, 0.253 mol) were placed inside a 250 mL Erlenmeyer flask with a long stir bar. THF (25 mL) and a crystal of I_2 were

[1] (a) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169. (b) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

added, and the mixture was stirred until the yellow iodine color had faded. More THF (75 mL) was then added. $CyCH_2Br$ (19.67 g, 0.111 mol) in 25 mL THF was added dropwise over 30 min. The reaction was then heated at 50 °C for 5 h. After cooling, the Gringard solution was filtered through a frit lined with Celite and titrated (86.6 mmol, 78% yield). $MePCl_2$ (5.04 g, 42.2 mmol) was diluted in 50 mL Et_2O in a 500 mL Erlenmeyer flask at -90 ºC. $CyCH_2MgBr$ solution in THF was added dropwise, and the reaction was stirred for 14 h, slowly warming to rt. The reaction was then filtered through a frit lined with Celite, quenched with 2 mL MeOH, and concentrated under reduced pressure. Upon precipitation of more salts, the filtrate was again filtered through a frit lined with Celite and concentrated under reduced pressure to a thick oil. The oil was flashed through a 2″-silica plug to obtain a pale-yellow oil (9.94 g, 98% yield). ^{1}H NMR (C_6D_6, 300 MHz) δ 1.87 (br dd, J = 27.6 & 11.7 Hz, 4H), 1.69 – 1.58 (m, 6H), 1.43 – 1.09 (m, 12H), 1.04 – 0.93 (m, 4H), 0.88 (d, $^2J_{H\text{-}P}$ = 2.1 Hz, 3H, CH_3P). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 41.0 (d, J = 13.4 Hz), 36.5 (d, J = 12.5 Hz), 36.0 (d, J = 8.8 Hz), 35.6 (d, J = 9.7 Hz), 27.2, 14.2 (d, J = 16.8 Hz). ^{31}P NMR (C_6D_6, 121 MHz) δ -53.5 ppm.

Synthesis of $LiCH_2P(CH_2Cy)_2$: To a 250 mL schlenk RB flask, ^{t}BuLi (1.7 M, 86.7 mmol) was added and concentrated under reduced pressure to dryness. $MeP(CH_2Cy)_2$ (17.48 g, 72.7 mmol) was added to the flask. The reaction was heated under a positive flow of N_2 at 90 °C for 4 h or until the reaction had completely solidified. The cream-colored solids were collected on a frit, mashed into a fine powder, and washed profusely with petroleum ether. (16.79 g, 94% yield). ^{31}P NMR (THF, 121 MHz) δ -28.5 ppm.

Synthesis of $[PhBP^{CH_2Cy}{}_3]Tl$: $LiCH_2P(CH_2Cy)_2$ (5.0690 g, 20.58 mmol) and

tmeda (2.3916 g, 20.58 mmol) were stirred together in 100 mL Et_2O and then chilled to -90 °C. $PhBCl_2$ (1.1232 g, 6.86 mmol) was diluted in 10 mL toluene and added dropwise to the solution. The reaction was stirred for 12 h, slowly warming to rt. The reaction was then filtered through a glass frit with Celite, and $TlPF_6$ (2.4706 g, 6.86 mmol) was added to the filtrate. The reaction was stirred for 12 h or until [$PhBP^{CH_2Cy}{}_3$]Li(tmeda) was consumed (^{31}P NMR: -37.6 ppm). The reaction was again filtered through a Celite-lined glass frit and and concentrated under reduced pressure to a goo. The goo was then taken up in minimal petroleum ether (~ 15 mL) to precipitate solids. The solids were collected on a frit, washed sparingly with petroleum ether, and washed profusely with CH_3CN. The petroleum ether filtrate can be stored at -30 °C to obtain a second crop of white solids that are similarly washed. (1.748 g, 25% yield). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.92 (br d, J = 6.0 Hz, 2H, H_o of Ph), 7.54 (t, J = 7.0 Hz, 2H, H_m of Ph), 7.28 (t, J = 7.0 Hz, 1H, H_p of Ph), 2.00 – 1.91 (m, 18 H), 1.75 – 1.58 (m, 30H), 1.31 – 1.23 (m, 18H), 1.18 – 1.02 (m, 18H). ^{13}C NMR (C_6D_6, 500 MHz) δ 168.1 (br m, C_{ipso} of BPh), 132.2, 127.8, 124.0, 39.5 (br), 36.7 (br), 36.0, 27.1, 27.0, 22.1 (m, CH_2PPh_2). ^{31}P NMR (C_6D_6, 121 MHz) δ 9.8 ppm (d, $J_{Tl\text{-}P}$ = 5570 Hz). Anal. Calcd. for $C_{51}H_{89}BP_3Tl$: C 60.63; H 8.88; N 0. Found: C 60.38; H 8.59; N <0.05.

Synthesis of [$PhBP^{CH_2Cy}{}_3$]FeCl, (1): [$PhBP^{CH_2Cy}{}_3$]Tl (3.2328, 3.20 mmol) and $FeCl_2$ (0.4138 g, 3.20 mmol) were stirred in 25 mL THF for 12 h. The reaction was filtered through Celite and concentrated under reduced pressure to dryness. The residue is then extracted with 1:1 THF/petroleum ether, filtered through glass wool, and concentrated to dryness. The yellow solids are washed profusely with petroleum ether (2.4509 g, 85%). Single crystals suitable for X-ray diffraction can be grown from an Et_2O

solution at -25 °C. ^{1}H NMR (C_6D_6, 300 MHz) δ 186.64, 40.16, 19.63, 18.05, 2.24, 1.22, 0.24, -0.39, -5.01, -5.62, -13.24, -16.37, -28.80, -39.98**.** Evans method (C_6D_6): 5.39 B.M. Anal. Calcd. for $C_{51}H_{89}BClFeP_3$: C 68.27; H 10.00; N 0. Found: C 67.89; H 9.77; N <0.05.

Synthesis of "[PhBP$^{CH_2Cy}{}_3$]Fe", (2): A 10 mL THF solution of [PhBP$^{CH_2Cy}{}_3$]FeCl (0.1119 g, 0.125 mmol) was stirred over sodium amalgam (0.4911 wt %, 0.131 mmol) with a glass stir bar for 2 to 3 h. The intense lime-green solution was then filtered through a Celite plug followed by a glass wool pipette. The solution can be used for reactions without further purification. Vapor diffusion of petroleum ether into the THF solution gave dark-green solids that tested analytically pure by combustion analysis. The ^{1}H NMR spectrum (THF-d_8) contains broad peaks ranging from -7 to 72 ppm. The peaks do not sharpen fully upon warming to 60 ºC. ^{31}P NMR (121 MHz, THF-d_8): δ -25.4 (br) ppm. UV-vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 1395 (470), 1016 (310), 743 (410). Anal. Calcd. for $C_{51}H_{89}BFeP_3$: C 71.08; H 10.41; N 0. Found: C 71.09; H 10.25; N 0.06.

Synthesis of [PhBP$^{CH_2Cy}{}_3$]Fe(PMe$_3$), (3): To an 8 mL THF solution of **2** (0.1114 mmol), PMe_3 (17.6 mL, 0.1649 mmol) was added via microsyringe, and within a few min, the solution changed from an intense lime-green to a pale-brown color. After stirring for 6 h, the solution was concentrated under reduced pressure to dryness. The residue was extracted with petroleum ether to give a pale-yellow-green solution, which formed pale-green crystals when stored at -30 °C (0.763 g, 72% yield). ^{1}H NMR (C_6D_6, 300 MHz) δ 87.74, 65.16, 11.56, 8.80, 8.72, 7.78, 4.97, 3.64, 3.14, 2.50, 1.20, 0.88, -11.59. UV-vis (C_6H_6) λ_{max}, nm (ε, M^{-1} cm^{-1}): 963 (990). Anal. Calcd. for $C_{51}H_{89}BFeP_4$: C 69.15; H 10.53; N 0. Found: C 69.65; H 10.68; N 0.14.

Synthesis of [PhBP$^{CH_2Cy}_3$]Fe(NAd), (4): To a 15 mL THF solution of **2** (0.2092 mmol), 1-adamantyl azide (35.6 mg, 0.2090 mmol) was added. Gradually, the reaction mixture turned from intense lime-green to burgundy. After 8 h, the solution was concentrated under reduced pressure to dryness, washed with petroleum ether (4 x 2 mL), and extracted with benzene. Vapor diffusion of petroleum ether into the benzene solution afforded dark-maroon crystals. (192.0 mg, 91% yield) ^{1}H NMR (C_6D_6, 300 MHz) δ 24.38, 17.80, 12.98, 9.59, 8.99, 6.32, 5.00, 3.99, 1.59, 1.29, 0.89, 0.63, -0.06, -0.23, -0.55, -0.91, -1.18, -8.58, -12.25. UV-vis (C_6H_6) λ_{max}, nm (ε, M^{-1} cm^{-1}): 509 (960), 415 (1290). Anal. Calcd. for $C_{61}H_{104}BFeNP_3$: C 72.46; H 10.37; N 1.39. Found: C 72.23; H 10.09; N 1.52.

Synthesis of {[PhBP$^{CH_2Cy}_3$]Fe}$_2$(μ-η^3:η^3-C_6H_6), (5): A 10 mL THF solution of **2** (0.1847 mmol) was concentrated under reduced pressure to dryness. The green residue was washed liberally with petroleum ether, extracted with benzene, filtered through a glass wool pipette, and concentrated under reduced pressure to a dark-green powder (0.155 g, 93% yield). Single crystals suitable for X-ray diffraction can be grown from toluene/petroleum ether at -30 °C. ^{1}H NMR (C_6D_6, 300 MHz) δ 8.05 (d, *J* = 6.9 Hz, 4H), 7.55 (t, *J* = 6.9 Hz, 4H), 7.27 (t, *J* = 6.9 Hz, 2H), 4.91 (br s, 6H, C_6H_6), 2.27 (br d, *J* = 10.2 Hz, 12H), 2.01 – 1.94 (m, 36H), 1.80 – 1.60 (m, 48H), 1.29 – 1.21 (m, 72H). ^{31}P NMR (C_6D_6, 121 MHz) δ 45.5 ppm. UV-vis (C_6H_6) λ_{max}, nm (ε, M^{-1} cm^{-1}): 681 (1090). Anal. Calcd. for $C_{108}H_{184}B_2Fe_2P_6$: C 71.99; H 10.29; N 0. Found: C 71.74; H 10.01; N <0.05.

Synthesis of {[PhBP$^{CH_2Cy}_3$]Fe}$_2$(μ-CO)(μ-O), (6): A 10 mL THF solution of **2** (0.1116 mmol) was transferred to a 50 mL reaction vessel with a Teflon-plug stopcock.

The solution was cooled in LN_2 and evacuated under high vacuum. The vessel was then attached to a gas bulb (55.39 cm^3). Gaseous CO_2 (18.5 cm Hg, 0.5578 mmol) was added to the bulb and condensed into the vessel using LN_2. After exposure to the gas, the vessel was sealed, and the reaction was allowed to warm to rt. Immediately, the solution turned a darker green color. After 6 h, the solution was evacuated under reduced pressure to dryness. The residue was extracted with benzene. Vapor diffusion of petroleum ether into the benzene solution afforded dark-green crystals (0.0641 g, 65% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 8.07 (d, *J* = 7.0 Hz, 4H), 7.54 (t, *J* = 7.0 Hz, 4H), 7.24 (t, *J* = 7.0 Hz, 2H), 2.31 (m, 12H), 2.05 (m, 24H), 1.95 (m, 24H), 1.71 (m, 24H), 1.56 (d, *J* = 10.5 Hz, 12H), 1.37 – 1.15 (m, 72H). ^{13}C NMR (126 MHz, C_6D_6): δ 164.6 (br), 132.1, 127.9, 124.7, 40.9, 37.8, 37.4, 36.2, 27.4, 27.0, 26.8, 13.8 (br m). ^{31}P NMR (121 MHz, THF): δ 51.9 ppm. IR(THF, KBr): ν(CO) = 1730 cm^{-1} (^{13}C-labeled: 1692 cm^{-1}). Anal. Calcd. for $C_{103}H_{178}B_2Fe_2O_2P_6$: C 69.98; H 10.15; N 0.0 Found: C 69.84; H 9.92; N 0.06.

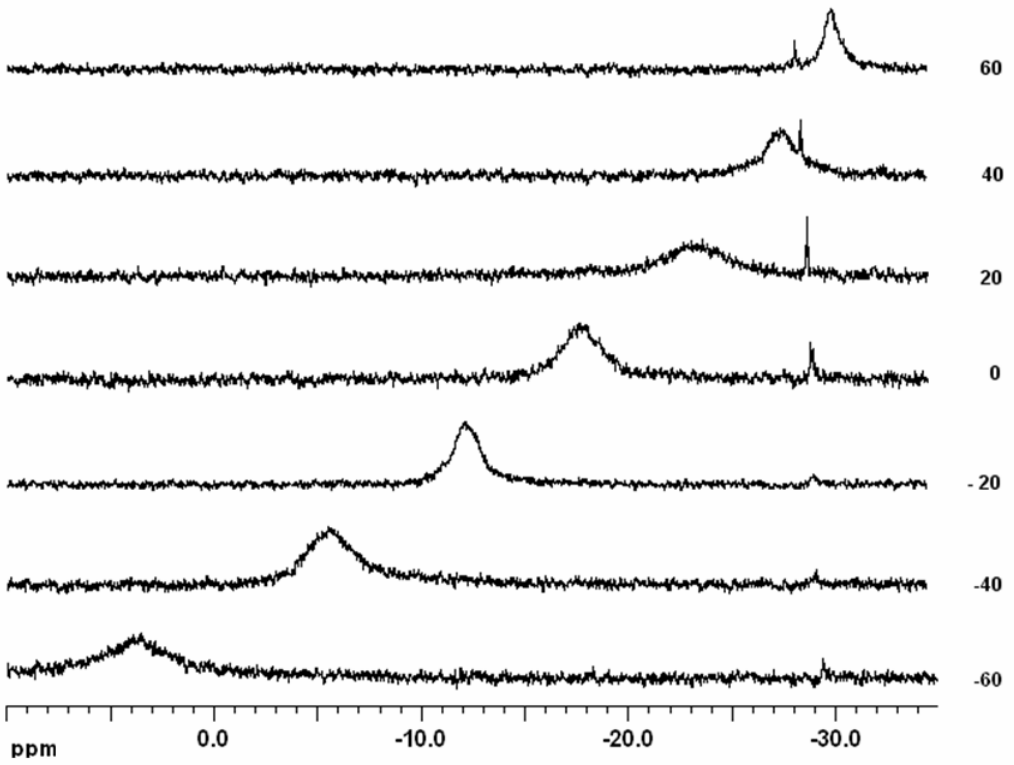

Figure 1. ^{31}P VT NMR spectra of "[PhBP$^{CH_2Cy}{}_3$]Fe" (**2**) in d_8-THF from -60 ºC to +60 ºC.

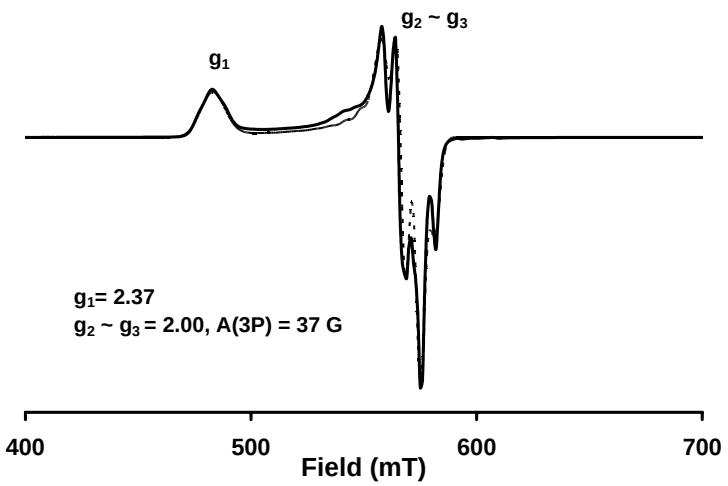

Figure 2. EPR spectrum of "[PhBP$^{CH_2Cy}{}_3$]Fe" (**2**) (THF glass at 4K, 9.37 GHz, X-band). Values for *g* and *A* were estimated by simulating the EPR spectrum (shown in dashed lines).

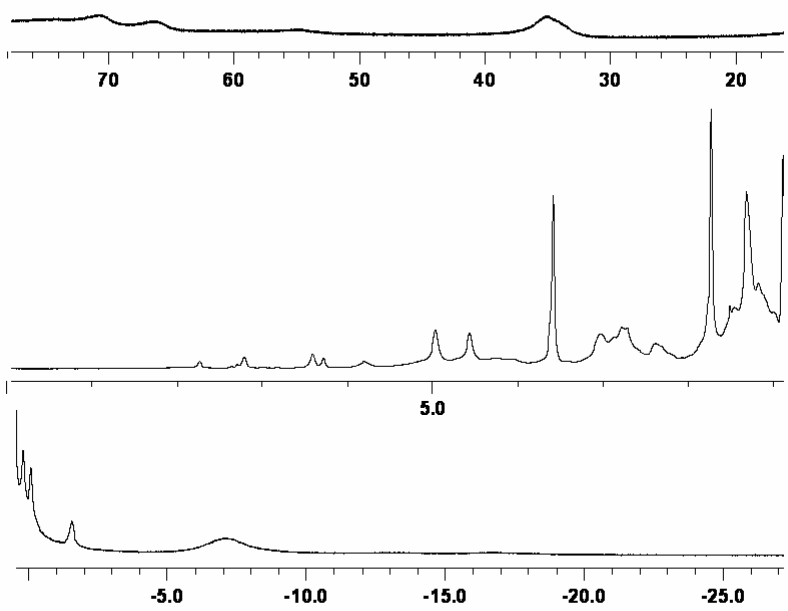

Figure 3. ^{1}H NMR spectrum for "[PhBP$^{CH2Cy}{}_3$]Fe" (**2**) in THF-d_8 at 60 °C.

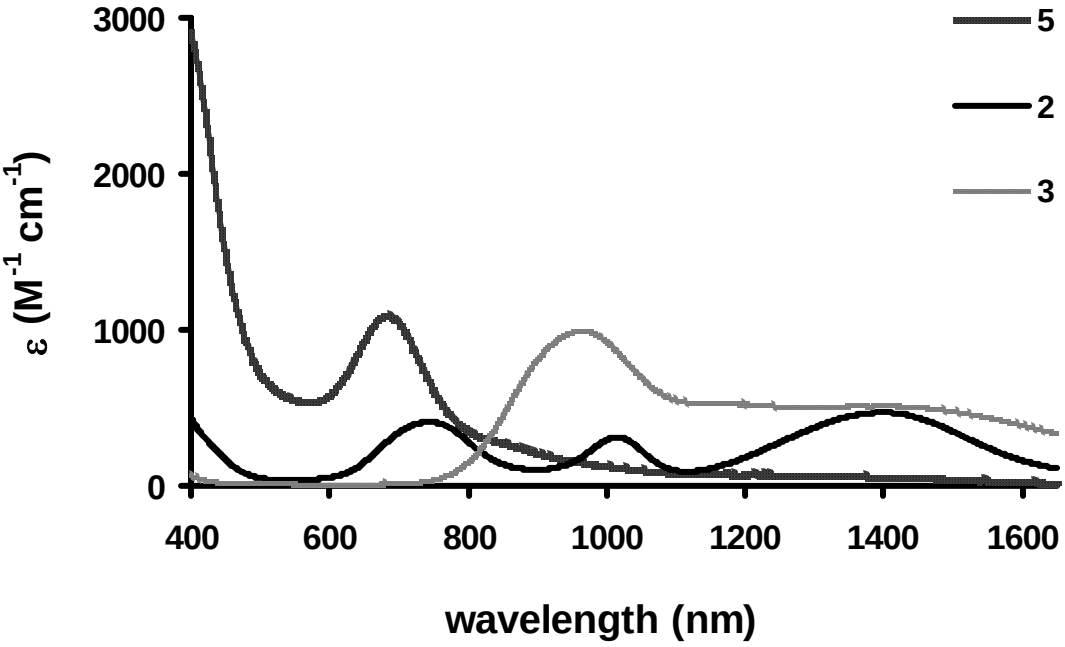

Figure 4. NIR data for "[PhBP^{CH_2Cy_3}]Fe" (**2**), [PhBP^{CH_2Cy_3}]Fe(PMe$_3$) (**3**), and {[PhBP^{CH_2Cy_3}]Fe}$_2$(μ-η^3:η^3-C$_6$H$_6$) (**5**) in THF.

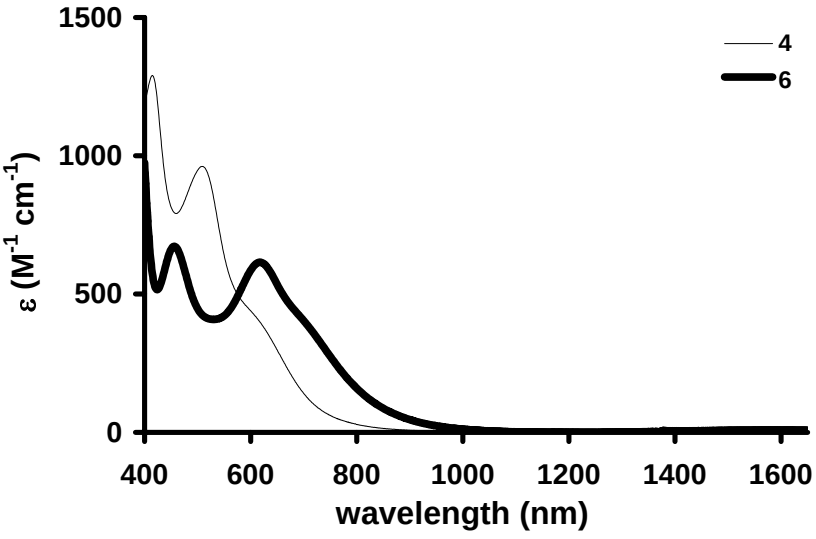

Figure 5. NIR data for {[PhBP^{CH_2Cy_3}]Fe}$_2$(μ-CO)(μ-O) (**6**) shown in bold and [PhBP^{CH_2Cy_3}]Fe(NAd) (**4**) in lighter trace.

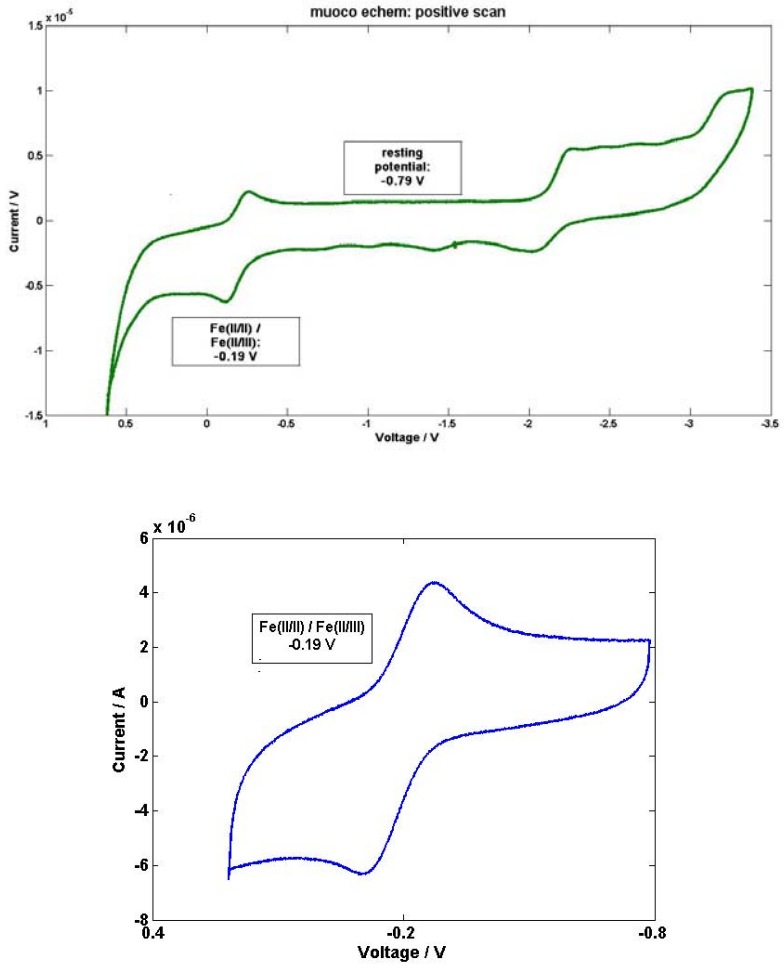

Figure 6. Electrochemical data for $\{[PhBP^{CH_2Cy}_3]Fe\}_2(\mu\text{-}CO)(\mu\text{-}O)$ (**6**). Top trace shows full scan and a reversible couple at ~ -0.2 V. The data centered around exclusively around this couple are shown in the bottom trace.

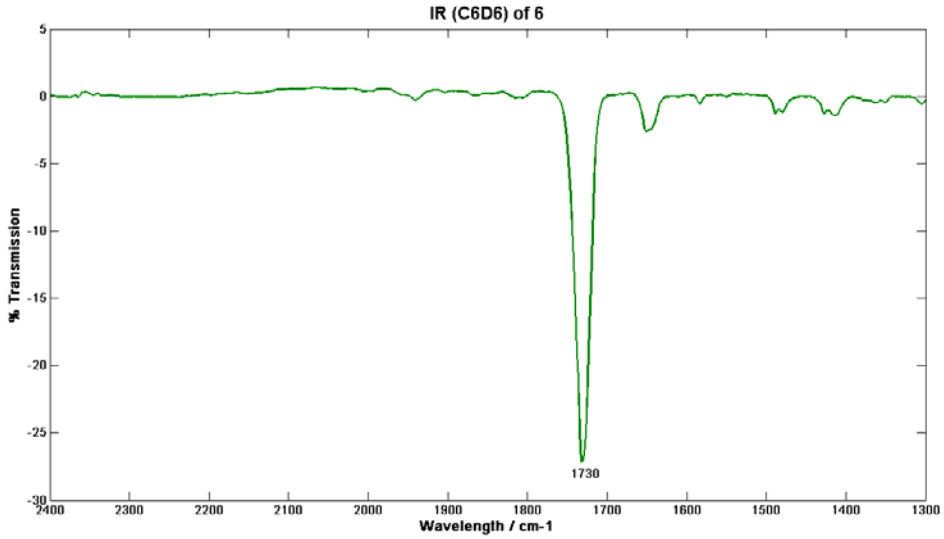

Figure 7. Solution IR spectrum (KBr/C_6D_6) of an isolated sample of complex **6**.

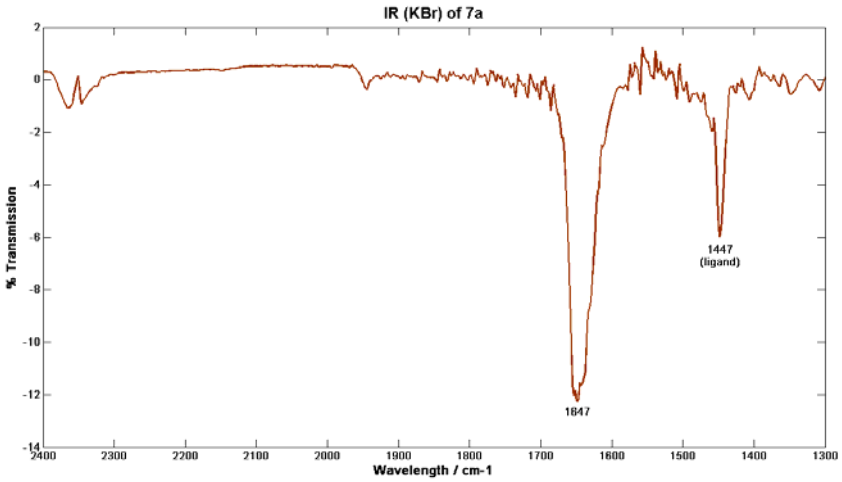

Figure 8. Solution IR spectrum (KBr/C_6D_6) of an isolated sample of complex **7a**.

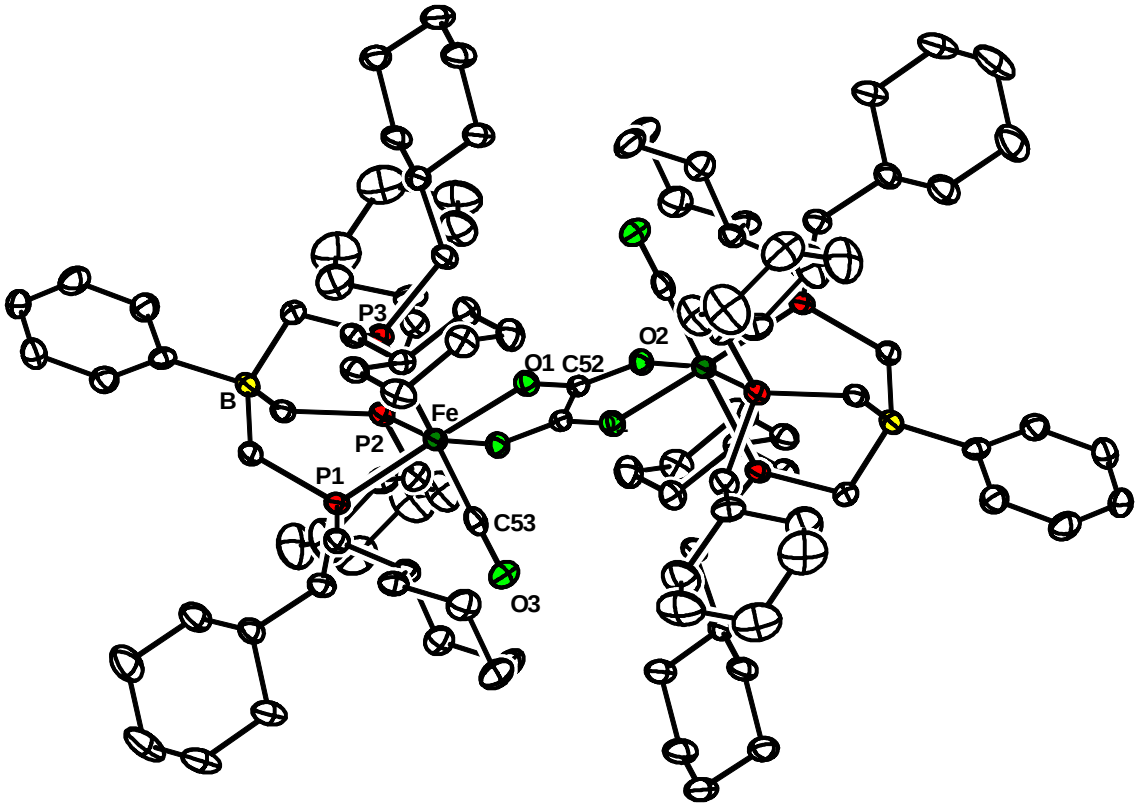

Figure 9. Anistropically refined X-ray structure of **7b** (ellipsoids at 50% probability). See CIF file for complete details.